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(54) [Title of the Invention] Anti- bacterial Polymer Particles and the Process for the Production Thereof

[57] [Abstract]

[Tasks]

To obtain anti- bacterial polymer particles having a high anti- bacterial activity, whose affinity to a resin is improved and whose coating characteristics are improved

[Means for Achieving the Objective]

Hydrophilic polymer particles (average particle diameters : from 0.1 nm to 100 μm) constituted with a hydrophilic polymer gel having a cross linked structure containing a hydrophilic unit containing nitrogen atoms, a unit having a functional group containing at least one atom selected from an oxygen atom, a nitrogen atom and a sulfur atom, and a cross linking unit are allowed to carry an anti- bacterial metal component (such

as a silver component) which can form a coordination bond with the above - mentioned functional group, thereby obtaining anti- bacterial polymer particles. For the above - mentioned functional group, a carboxyl group, an amino group, an imino group, a mercapto group, etc. can be included. The amount of carrying of such an anti- bacterial metal component is about 0.01 to 70 % by weight when converted into a metal component. The anti- bacterial particles has high affinity to a resin, and is useful as an anti- bacterial resin composition (resin composition for coating).

[What we claim is]

[Claim 1]

Anti- bacterial polymer particles in which an anti- bacterial metal component constituted with a metal ion or a metal compound is chemically bound to and carried by, polymer particles,

said anti- bacterial polymer particles characterized in that the above -

mentioned polymer particles are constituted with a hydrophilic polymer having a cross linking structure including a hydrophilic unit, a unit having a functional group containing at least one atom selected from an oxygen atom, a nitrogen atom and a sulfur atom, which can be chemically bound with the anti- bacterial metal component, and a cross linking unit .

[Claim 2]

Anti- bacterial polymer particles, in accordance with Claim 1, characterized in that the hydrophilic polymer having a cross- linking structure is constituted with a hydrophilic polymer gel containing a hydrophilic unit containing nitrogen atoms, a unit containing at least one functional group selected from a carboxyl group, a pyridyl group, and a mercapto group, and having a functional group which can be chemically bound with an anti- bacterial metal component, and a cross linking unit.

[Claim 3]

Anti- bacterial polymer particles, in accordance with Claim 1. characterized in that the average particle diameters of the polymer

particles are from 0.1 nm to 100 μm.

[Claim 4]

Anti- bacterial polymer particles, in accordance with Claim 1. characterized in that the anti- bacterial metal component is at least one metal component selected from a group consisting of silver, platinum, copper, zinc, nickel, cobalt, molybdenum, and chromium.

[Claim 5]

Anti- bacterial polymer particles, in accordance with Claim 1. characterized in that the amount of carrying of such an anti- bacterial metal component is about 0.01 to 70 % by weight when converted into a metal component.

[Claim 6]

Anti- bacterial polymer particles, in accordance with Claim 1. characterized in that they are constituted with hydrophilic polymer particles with average particle diameters of the polymer particles are from 0.1 nm to 100 μm, containing a nitrogen – containing hydrophilic unit, a unit including an oxygen – containing functional group, a nitrogen-

containing functional group, or a sulfur –containing functional group and a cross- linking unit, and an anti- bacterial silver component which is chemically bound to and carried by, the above - mentioned functional group / groups of the polymer particles, and that the amount of carrying of the anti- bacterial silver component is 1 to 50 % by weight with respect to the whole in terms of silver conversion.

[Claim 7]

A process for the production of anti- bacterial polymer particles in which an anti- bacterial metal component constituted with a metal ion or a metal compound is allowed to be chemically bound to and carried by a functional group / groups of hydrophilic polymer particles which contain at least one atom selected from a group consisting of an oxygen atom, a nitrogen atom, a sulfur atom or a phosphor atom and which have a cross linking structure.

[Claim 8]

A resin composition containing the anti- bacterial polymer particles in accordance with Claim 1 and a resin / resins.

[Claim 9]

A process for the production of an anti- bacterial resin composition in which the anti- bacterial polymer particles in accordance with Claim 1 and a resin / resins are mixed.

3. Detailed Explanation of the Invention

[0001]

[Technology Field to which the Invention Belongs]

The present invention relates to anti- bacterial polymer particles which display effectively an anti- bacterial property against various types of microorganisms (bacterium, fungus, etc.), and a process of the production thereof, and an anti- bacterial resin composition which contains the above - mentioned anti- bacterial polymer particles and is useful as a coating agent.

[0002]

[Conventional Technology]

In recent years, anti- bacterial treatments have been being considered on

various products. This anti- bacterial treatment is usually applied by kneading and mixing an organic anti- bacterial agent or an inorganic anti-bacterial agent in a plastic or by coating a product with a coating containing an anti- bacterial agent. Between the above - mentioned anti-bacterial agents, organic anti- bacterial agents are excellent in anti-bacterial property, immediate effectiveness, and dispersion property in a resin. However, there are problems such as elution from a base material, heat resistance, and safety to human bodies as well as appearance of drug resistance of microorganisms. On the other hand, inorganic anti- bacterial agents obtained by allowing an inorganic carrier (such as particular inorganic carrier such as zeolite, and silica gel) to carry a metal ion (silver, zinc, copper, etc.) having an anti- bacterial activity are excellent in various aspects : for example, heat resistance, broad anti- bacterial spectra, a difficulty in acquiring drug resistance, and safety to human bodies, and thus they are currently main streams of anti- bacterial agents. Here as the anti- bacterial activity of an anti- bacterial agent is displayed at the surface of a product anti- bacterially treated, in order to effectively

utilize an anti- bacterial agent, it is effective to coat the surface of a product with an anti- bacterial agent.

[0003]

However, when an inorganic anti- bacterial agent is applied for coating the surface of a base material, there arise various problems. For example, as an inorganic anti- bacterial agent basically uses hydrophilic zeolite, silica gel, etc. as a carrier, when blended with a coating agent, i) it is difficult to uniformly disperse an anti- bacterial agent in a coating agent, ii) as the diameters and specific gravity of carrier particles are relatively large, they tend to precipitate in a coating agent, and therefore, it is necessary to blend a large amount of an anti- bacterial agent in order to increase the contact frequency with microorganisms and to allow a sufficient anti- bacterial effect to be displayed, furthermore iii) as the affinity and adhesion to an organic binder, an anti- bacterial agent tends to come off from the surface of a coating film, and the mechanical strength of a coating film is reduced, and iv) the transparency of a coating film is reduced. Furthermore, there is a case in which it is colored by the

irradiation with ultraviolet light or light.

[0005]

On the other hand, there has been proposed an anti- bacterial agent in which silver ion is carried on an organic polymer. In the Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 2 / 1990 – 288804, a deodorizing anti- bacterial composition which contains an aqueous solution or a dispersion solution of a carboxyl group – containing polymer and a silver ion is disclosed. The Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 4 / 1992 – 173712, there is a disclosure of an anti- bacterial agent a silver ion is allowed to be carried on the surfaces of acryl polymer particles sulfonic acid group (note by translator: something seems to be missing). In Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 8 / 1996 – 151310, an anti- bacterial agent constituted with a combination of a maleic acid polymer and a silver ion is disclsoed, and in Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 8 / 1996 – 165212, there is disclosed an anti- bacterial agent constituted with (metha) acrylic acid ester – (metha)

acrylic acid – silver polymer particles. However, with these anti- bacterial agents, silver ion is eluted in an early stage, and thus it is impossible to retain a high degree of an anti- bacterial activity for an extended period of time. Especially, under a high humidity environment or a watery environment under which recent (sic : probably a mistake of bacteria) and microorganisms tend to multiply, the anti- bacterial activity can not be effectively displayed, and the retention thereof is not sufficient.

[0005]

[Problem Points which the Invention Tries to Solve]

Therefore, a purpose of the present invention is to provide anti- bacterial polymer particles which can retain and display an anti- bacterial activity for a long period of time in spite of the fact that use is made of an inorganic anti- bacterial metal component and an anti- bacterial composition containing the anti- bacterial polymer particles, and a process for the production thereof. Another purpose of the present invention is to provide anti- bacterial polymer particles which can effectively display the anti- bacterial activity as humidity and a water

content increase, and have environmental adaptability and an anti-bacterial composition containing the anti- bacterial polymer particles, and a process for the production thereof. Another purpose of the present invention is to provide anti- bacterial polymer particles which are excellent in dispersion property, affinity to organic polymers and coating retention property when used as a resin composition such as a coating agent and an anti- bacterial composition containing the anti- bacterial polymer particles, and a process for the production thereof.

[0006]

[Means by which to Solve the Problem Points]

The inventors of the present invention have found, as a result of extensive studies and investigations, that when a carrier of an organic polymer having a hydrophilic unit is allowed to carry an anti- bacterial metal component, an anti- bacterial resin composition which can release the anti- bacterial metal component depending on a humidity environment, can maintain a high degree of an anti- bacterial activity for a long period of time, has a high degree of affinity to organic polymers, and is useful as

an anti- bacterial coating, etc., thereby achieving the present invention. That is, the anti- bacterial polymer particles in accordance with the present invention is such that an anti- bacterial metal component made of a metal ion or a metal compound is chemically bound to and carried by, polymer particles. In the anti- bacterial polymer particles, in general, the anti- bacterial metal component is chemically bound to the polymer particles through a functional group / groups containing at least one atom selected from a group consisting of an oxygen atom, a nitrogen atom and a sulfur atom. That is, the polymer particles which constitute an anti-bacterial polymer are constituted with a hydrophilic polymer having a cross linking structure, containing a hydrophilic unit, a unit having a functional group / groups which contains / contain at least one atom selected from a group consisting of an oxygen atom, a nitrogen atom and a sulfur atom and which can be chemically bound to an anti- bacterial metal component, and a cross linking unit. The average particle diameters of the polymer particles are from about 0.1 nm to 100 μm. As the above - mentioned anti- bacterial metal components, mention may be made of

silver, platinum, copper, zinc, nickel, cobalt, molybdenum, and chromium. The amount of carrying of such an anti- bacterial metal component is about 0.01 to 70 % by weight when converted into a metal component. The above - mentioned anti- bacterial polymer can be produced by allowing an anti- bacterial metal composition made of a metal ion or a metal compound to be chemically bound to and carried by, a functional group / groups of hydrophilic polymer particles having a cross linking structure. The resin composition in accordance with the present invention contains the above - mentioned anti- bacterial polymer particles and a resin (such as a binder resin), and can be utilized as an anti- bacterial coating resin composition. This anti- bacterial resin composition can be prepared by mixing the above - mentioned anti- bacterial polymer particles and a resin (such as a binder resin).

[0007]

In this Specification, "carrying" of an anti- bacterial metal component means that an anti- bacterial metal component is retained on the surface of polymer particles and /or in them, as long as the anti- bacterial

property can be displayed. "Chemical binding" or "chemically bound" means both ion binding and coordination binding, and in some cases, simply "coordinated" might be used. In addition, a "non- cross linking hydrophilic polymer" and "hydrophilic polymer having a cross linking structure" may be called simply "hydrophilic polymer".

[0008]

[Mode of Working of the Invention]

[Hydrophilic polymer particles] The polymer particles are constituted with a hydrophilic polymer having a functional group / groups to which an anti- bacterial metal component can be coordinated, and may be either a synthetic polymer or a natural polymer. The hydrophilic polymer particles have a cross linking structure, and are in general either difficult to be dissolved or impossible to be dissolved in a solvent. The hydrophilic polymer particles which function as a carrier contain a hydrophilic unit and at least one atom selected from an oxygen atom, a nitrogen atom and a sulfur atom, and are further constituted with a coordination unit having a functional group / groups (especially coordination group) which can be

chemically bound to an anti- bacterial metal component, and a cross linking unit. Here in the hydrophilic polymer particles, the hydrophilic unit and the coordination unit having a functional group / groups can be of the same type or different.

[0009]

As a hydrophilic unit, use may be made of various types of hydrophilic segments or fragments, and for example, mention may be made of a carboxyl group – containing unit [unit formed with a monomer containing a carboxyl group or an acid anhydride such as (metha) acrylic acid and maleic anhydride], a hydroxyl group – containing unit [unit formed with a monomer containing a hydroxyl group / groups such as a vinyl alcohol unit generated by hydrolysis of vinyl acetate, hydroxyl C_{2-3}, and an alkyl (metha) acrylate], an ether group – containing unit [unit formed with an ether group - containing monomer such as vinyl C_{1-4}, alkyl ether, poly ethylene glycol mono or di (metha) acrylate and poly ethylene glycol], a nitrogen – containing unit [a unit formed with a nitrogen – containing monomer such as vinyl pyrolidone, vinyl pyridine,

(metha) acryl amide, methylol (metha) acryl amide, N, N- dialkyl amino alkyl (metha) acrylate, etc. A hydrophilic polymer may contain a plurality of different hydrophilic units, and hydrophilic units mat, if necessary, form a salt.

[0010]

As to preferable hydrophilic units, a hydrophilic unit which forms a water – soluble polymer and has affinity to a hydrophobic resin, may be included, and as such a hydrophilic unit, mention may be made of a unit containing a nitrogen atom (especially, an amide group or an N – substitution amide group) (for example, a hydrophilic unit which can be formed with (metha) acryl amide, N – substitution (metha) acryl amide, etc.). As an N- substitution (metha) acryl amide, for example, mention may be made of an N - C_{1-9} alkyl (metha) acryl amide such as N – methyl (metha) acryl amide, N – ethyl (metha) acryl amide, and N- butyl (metha) acryl amide, an N - C_{1-6} acyl (metha) acryl amide, etc. Here if a hydrophilic unit is formed with an N - C_{1-6} alkyl (metha) acryl amide such as N – butyl acryl amide, it is possible to render a warm feel to

polymer particles.

[0011]

With a coordination unit, as a functional group containing an oxygen atom (especially, coordination group), for example, mention may be made of a carboxyl group or a derivative group thereof (an acid halide group, an acid anhydride group, etc.), a hydroxyl group, an acyl group (a C_{1-4} acyl group such as formyl group, and acetyl group), a carbonyl group, a poly carbonyl group containing an acetyl acetone structure, an ether group, a crown ether group, an aromatic poly hydroxyl group containing a catechol structure, an aromatic hydroxyl carbonyl group containing a salicylic acid structure, a poly carboxylic acid containing a phthalic acid structure, an epoxy group, an oxygen – containing heterocyclic group(furil group, chromanyl group, etc.), etc.

[0012]

As a functional group (especially a coordination group) which contains a nitrogen atom, for example, mention may be made of an amino group, a mono - or di- alkyl amino group (mono C_{1-4} alkyl amino group, di - C_1

$_{-4}$ alkyl amino group, etc.), an azo group, an amizino group, a hydrazino group, a hydrazono group, a cyano group, a nitrogen- containing heterocyclic group (a pyrolyl group, an imidazolyl group, a pyridyl group, a bi-pyridyl group, a pyrrolyl group, a piperidinyl group, a piperadinyl group, a quinolyl group, a benzimidazolyl group, a phenan throlyl group, etc.), an aza- crown ether group, etc. As a nitrogen – containing functional group, an amino group or an imino group are often used, however, a nitrogen – containing group may be a heterocyclic group such as a pyridyl group.

[0013]

As a functional group which contains a nitrogen atom, (especially, a coordination group), mention may be made of a mercapto group (thiol group), a thioxo group, a thienyl group, a thio acetyl group, an alkyl thionyl group, thio carbamoyl group, a sulfonyl group, a thio carboxyl group, a sulfonic acid group (sulfo group), sulfinic acid group (sulfino group), a thio urea group (tho ureide group), a thio crown ether group, a thio ether group, a heterocyclic group (such as a thio phenyl group), etc.

[0014]

Hydrophilic polymer particles may have a functional group / groups having a plurality of atoms selected from an oxygen group, a nitrogen group and a sulfur group, for example, a functional group containing an oxygen atom and a nitrogen atom. As such a functional group, for example, mention may be made of a nitro group, a ureide group, an amino alcohol group such as an amino hydroxyl ethyl group, an amino phenyl group, a quinolino group, an amino poly carboxylic acid group such as an imidino acetic acid group, an oxime group, an amide oxime group, a heterocyclic group (such as a morpholino group and a morphonyl group).

[0015]

The above - mentioned functional groups can be combined in a plurality of them. As the bonding strength with a metal ion or a metal compound varies depending on a type of a functional group, it is possible to control the release of an anti- bacterial metal component from hydrophilic polymer particles by combining a plurality of functional groups of

different types.

[0016]

The types of functional groups can be selected depending on the types of anti- bacterial metal components. As preferable functional groups, oxygen- containing functional groups [for example, a carboxyl group, etc.], nitrogen – containing functional groups [for example, nitrogen – containing functional groups (an imidazolyl group, a pyridyl group, a bi-pyridyl group, etc.), etc.], and a sulfur – containing functional groups [a thiol group, a thio ureide group, etc.]. When such functional groups and an anti- bacterial metal component (such as silver) are combined, a complex can be effectively formed.

[0017]

As for a cross linking unit by which to introduce a cross linking structure into hydrophilic polymer particles, it is permissible to constitute it with a condensation group or fragment such as self cross linking polymer particles (for example, setting of a thermal setting resin or cross linking particles), or with a cross linking agent. The cross linking polymer

particles are high in heat resistance and displays high resistance even when exposed to a high temperature (for example, about 300 °C) like in a case of a baking coating. As a cross linking agent which constitutes a cross linking unit, in the case of a polymer (vinyl polymerization type polymer) which uses a polymerizable unsaturated monomer as a raw material, in general, use is made of multi- functional polymerizable monomers [such as di-vinyl benzene, methylene bis (metha) acryl amide, ethylene glycol di (metha) acrylate, di- ethylene glycol di (metha) acrylate, propylene glycol di (metha) acrylate, di- propylene glycol di (metha) acrylate, tri- methylol propane tri (metha) acrylate, penta - erythrotol tri- or tetra – (metha) acrylate, etc.].

[0018]

In a case of a hydrophilic polymer (condensation type or addition condensation type polymer) which uses a condensation or addition reactive monomer as a raw material, it is possible to use, as a cross linking agent, a compound which has 2 or more reactive functional groups with respect to the functional group of the polymer. In a case in

which a hydrophilic polymer has a plurality of carboxyl groups or an acid anhydride group, for example, as a cross linking agent, mention may be made of a multi valence metal ion (such as magnesium ion, aluminum ion, and zirconium ion); poly iso-cynate; polyamine; an epoxy compound having a plurality of epoxy groups; bis oxazoline compound, etc. In a case in which a hydrophilic polymer has a hydroxyl group, for example, as a cross linking agent, mention may be made of poly iso- cyanate; a multi- valence carboxylic acid or a reactive derivative thereof (acid halide, and acid anhydride); a compound having a hydrolysis silyl group (dichloro dimethyl silane, dichloro tetra- methyl di- siloxane, methyl tri- methoxy silane, methyl tri- ethoxy silane, etc.); a compound having a plurality of methylol groups or alkoxy methyl groups (urea resin, melamine resin, etc.); bis oxazoline compound, etc. In a case in which a hydrophilic polymer contains an amino group, an amide group, etc., for example, as a cross linking agent, use may be made of poly iso- cyanate, a multi valence carboxylic acid or a reactive derivative thereof; a compound having a hydrolysis silyl group; an epoxy compound having a

plurality of epoxy groups; bis oxazoline compound, etc.

[0019]

The degree of cross linkage of hydrophilic polymer particles is 0.1 to 30 % by weight when converted into a cross linking unit (or cross linking agent), preferably 0.5 to 20 % by weight and more preferably 1 to 10 % by weight.

[0020]

Hydrophilic polymer particles having a cross linking structure include (1) a copolymer or a co- condensation product of the above - mentioned coordination unit having a hydrophilic property (for example, the above - mentioned unit formed with a monomer / monomers containing a carboxyl group, a nitrogen – containing group such as a nitrogen – containing heterocyclic group, a mercapto group, etc.) and a cross linking unit (for example, a unit formed with a cross linking unit such as a multi-functional polymerizable monomer, and a cross linking agent), (2) a copolymer or a co- condensation product of the above - mentioned hydrophilic unit (a unit formed with (metha) acryl amide, N- (substitution

(metha) acryl amide, etc.), the above - mentioned coordination unit (for example, the above - mentioned unit formed with a monomer / monomers containing a carboxyl group, a nitrogen – containing group, a mercapto group, etc.) and a cross linking unit (for example, a unit formed with a multi- functional polymerizable monomer).

[0021]

These hydrophilic polymer particles may contain, as a copolymerization unit, for example, a (metha) acryl series monomer such as a (metha) acrylic acid alkyl ester and (metha) acrylnitrile, an aromatic vinyl monomer such as styrene, a vinyl ester series monomer such as vinyl acetate, a halogen- containing monomer such as poly vinyl chloride, and poly vinylidene chloride, an olefine such as ethylene and propylene, etc., and if necessary, they may be modified.

[0022]

Preferable hydrophilic polymer particles can be constituted with a hydrophilic polymer gel [for example, a cross linking polymer having a coordination unit (cross linking poly acrylic acid, cross linking poly vinyl

pyridine, etc.), a cross linking polymer having an acryl amide unit and a coordination unit (an acryl amide – (metha) acrylic acid copolymer having a cross linking structure, an acryl amide – vinyl pyridine copolymer having a cross linking structure, an acryl amide – mercapto methyl substitution styrene copolymer having a cross linking structure, an acryl amide – (metha) acrylic acid – vinyl pyridine copolymer having a cross linking structure, etc.)].

[0023]

The concentration of the functional group (coordination unit) of hydrophilic polymer particles can be selected depending on a carrying amount of an anti- bacterial metal component, and for example, it is about 0.01 to 10 milli mol per 1 g of polymer particles, preferably, about 0.1 to 5 milli mol. Here, the amount of use of a monomer having a coordination unit can be, for example, chosen from a range of about 5 to 100 % by weight, preferably about 10 to 100 % by weight, and more preferably about 25 to 100 % by weight.

[0024]

In order to allow the anti- bacterial activity of an anti- bacterial metal component to be effectively displayed, the hydrophilic polymer particles can be porous. The specific surface area of the porous particles is, for example, about 10 to 1000 m^2 / g, preferably about 50 to 1000 m^2 / g, and more preferably about 25 to 1000 m^2 / g.

[0025]

The configuration of particular hydrophilic polymer can be spherical, plate- like, a rod –like, or petal –like, etc. The average particle sizes of hydrophilic polymer particles are, for example, about 0.1 nm to 100 μm, preferably about 1 nm to 30 μm (for example, 1 nm to 5 μm), and more preferably about 5 nm to 10 μm (especially 10 nm to 1 μm), and can be about 10 to 500 nm. The particle sizes of the hydrophilic polymer particles can be selected depending on use, however, if use is made of polymer particles of a nano size, it becomes possible to increase the dispersability thereof in a resin composition and the content of the anti-bacterial metal component in a resin composition, and thus a high degree of anti- bacterial activity can be displayed at a low addition quantity.

Furthermore, it becomes possible to control the release of an anti-bacterial metal component depending on the surrounding environmental humidity, by controlling the carrying state of the anti- bacterial metal component on hydrophilic polymer particles (for example, introduction of a plurality of functional groups having different coordination properties with respect to an anti- bacterial metal component into polymer particles by copolymerization, etc.), the mixing of a plurality of polymer particles having different functional groups and the degree of affinity of polymer particles to water (for example, a hygroscopic property and a swelling property of polymer particles), and thus an anti- bacterial agent having a swift acting property and a long lasting peroperty can be obtained.

[0026]

[Anti- bacterial metal component] An anti- bacterial metal component is chemically bound to, and carried by, the hydrophilic polymer particles. Especially, the anti- bacterial metal component is chemically bound to the hydrophilic polymer particles through the above - mentioned functional groups (functional groups containing an oxygen atom, a nitrogen atom, a

sulfur atom, a phosphor atom, etc.). The anti- bacterial metal component can be constituted with a metal ion or a metal compound having an anti-bacterial property and these anti- bacterial metal components can be used alone or in a combination of 2 or more of them. As a metal ion which has an anti- bacterial property, for example, mention may be made of a silver ion (silver (I) ion or silver (II) ion), a platinum ion, a copper ion, a zinc ion, a nickel ion, a cobalt ion, a molybdenum ion, and a chromium ion. As to preferable anti- bacterial metal ions, mention may be made of a silver (I) ion, a copper ion, and a zinc ion, but the silver ion is especially preferable.

[0027]

As a metal compound which has an anti- bacterial property, for example, mention may be made of a metal compound of at least one type of a metal selected from silver, platinum, copper, zinc, nickel, cobalt, molybdenum , and chromium, and in general, use can be made of a metal compound which is reactive or coordinative to the functional groups of the above - mentioned polymer. The above - mentioned metal compounds

can be metal complex compounds, and the metal complex compounds can be anionic, cationic or neutral. In a case of an anionic complex, it is preferable for a pairing cation to be a quaternary ammnonium having an anti- bacterial property (such as phenyl dimethyl alkyl ammonium, didecyl dimethyl ammonium, cetyl tri- methyl ammonium, and tetra-methyl ammonium).

[0028]

Preferable metal compounds include a silver compound such as a halogenated silver (AgCl, AgBr, etc.), a halogenosalt and a perhalogenosalt ($AgClO_4$, $AgClO_3$, $AgBrO_3$, $AgIO_3$, etc.), an inorganic acid salt (silver sulfate, silver nitrate, silver carbonate, etc.), an organic acid salt (silver acetate, silver oxalate, etc.), a complex (a di- cyano complex, a di thio sulfide complex, a di- anmin (sic) complex, a di-chloro complex, etc.). The above - mentioned anti- bacterial metal component (such as a silver component) may be coordinated to the functional group / groups of the above - mentioned polymer, thereby forming a complex (such as a thiol complex, a thio ureide complex, a

pyridyl complex, a bi- pyridyl complex, a phenan throlyl complex, and a histidil complex). When use is made of an anti- bacterial metal component which can be coordinated to a functional group / groups of a polymer, it becomes possible to increase the content of an anti- bacterial metal component, and to retain the anti- bacterial activity for a long period of time. In addition, even if the anti- bacterial activity is reduced, it can be easily regenerated just by immersing in an aqueous solution which contains an anti- bacterial metal ion.

[0029]

The carrying quantity of an anti- bacterial metal component can be any within a range to maintain the anti- bacterial activity, and for example, in terms of a metal conversion, it may be about 0.01 to 70 % by weight with respect to the total weight of hydrophilic polymer particles, preferably about 0.1 to 50 % by weight and more preferably about 1 to 40 % by weight. Especially about 5 to 40 % by weight is preferable.

[0030]

As a preferable anti- bacterial agent in the present invention, for example,

mention may be made of an anti- bacterial agent constituted with hydrophilic polymer particles with average particle sizes of hydrophilic polymer particles of about 1 nm to 10 μm (for example, 1 nm to 3 μm, preferably about 10 to 500 nm, especially about 50 to 500 nm), having a nitrogen – containing hydrophilic unit, a coordination unit such as an oxygen- containing group, a nitrogen –containing group, and a sulfur-containing group, and a cross linking unit, and an anti- bacterial silver component chemically bound (especially by the coordination bond) to and carried by, the above - mentioned functional groups of the polymer particles. With this anti- bacterial agent, the carrying quantity of the anti-bacterial silver component is, in terms of a silver conversion, about 1 to 50 % by weight with respect to the whole (preferably 5 to 40 % by weight). Here, in order to increase the anti- bacterial activity, the hydrophilic polymer particles may contain an organic anti- bacterial agent / agents, if necessary.

[0031]

[Process for the production of anti- bacterial polymer particles] The

anti- bacterial agent in accordance with the present invention can be prepared by allowing an anti- bacterial metal component to be chemically bound to and carried by, the functional group /groups of hydrophilic polymer particles. The above - mentioned hydrophilic polymer particles can be prepared by a conventional process such as crushing and sieving, suspension polymerization and emulsion polymerization. As a typical preparation process of cross linking hydrophilic polymer particles, mention may be made of a precipitation polymerization process : for example, a process in which by utilizing a polymerization initiating agent in a non- aqueous solvent (especially a mixture solution of water and a hydrophilic solvent), a monomer mixture consisting of a monomer corresponding to a coordination unit, a monomer corresponding to a hydrophilic unit, and a cross linking agent by which to form a cross linking structure. With this process, it is possible to control particle diameters of hydrophilic polymer particles by adjusting a type of a hydrophilic solvent and a ratio between water and a hydrophilic solvent, and thus it is possible to produce efficiently hydrophilic polymer particles

have particle diameters of a nano order. As a hydrophilic solvent, mention may be made of an alcohol such as methanol, ethanol, iso-propanol, and butanol, a ketone such as acetone, an ether such as dioxane and tetra- hydro furan, and a mixture solvent thereof. The ratio of mixing of water and a hydrophilic solvent can be appropriately selected from a range of , for example, the former / the latter = about 1 / 99 to 70 / 30 (% by weight) ; preferably about 3 / 97 to 50 / 50 (% by weight). With this precipitation polymerization process, particle sizes produced can be controlled without using especially a dispersion stabilizing agent, washing and recovery of particles are simple and easy, and it is possible to obtain hydrophilic polymer particles at a low cost.

[0032]

In addition, cross linking hydrophilic polymer particles can be obtained by a process in which a solution of a hydrophilic polymer containing a functional group / groups to which an anti- bacterial metal component can be coordinated, is added to and mixed with, a poor solvent, thereby forming polymer particles in the solvent, and then a cross linking agent is

added thereto, thereby setting them; a process in which a mixture solution of a cross linking agent and a hydrophilic polymer is added to and mixed with, a poor solvent with respect to the polymer, and thus polymer particles are formed in the solvent, followed by setting; a spray dry process in which a mixture of a cross linking agent and a hydrophilic polymer is sprayed and dried, etc. Here cross linking hydrophilic polymer particles of a thermosetting resin having a self- cross linking property can be prepared similarly to what has been described above, without using a cross linking agent.

[0033]

Here the functional group to which an anti- bacterial metal component can be chemically bound, may be derived from the above - mentioned monomers which become a raw material for a polymer and a cross linking agent, and can be introduced in a polymer produced by utilizing a polymer reaction, etc. As a process by which to introduce the above - mentioned functional group into a polymer by use of a polymer reaction, for example, use may be made of a conventional process similar to a

preparation process of a metal ion adsorption resin such as a chelate resin. For example, a mercapto group, and a bi -pyridyl group can be introduced according to the process described in Ueyama, N. et al: Inorg. Chem. Acta. 89, 19 – 23 (1984). An imidazol group can be introduced, for example, by allowing a polymer having a chloro methyl group and for example, histidin to react with each other.

[0034]

An anti- bacterial metal component can be carried on polymer particles, for example, by a process in which polymer particles are, if necessary, swollen with a solvent, a solution containing an anti- bacterial metal component is added thereto and mixed therewith, and the anti- bacterial metal component is allowed to be chemically bound to the polymer. After carrying the anti- bacterial metal component, the polymer is washed, and dried, and thus anti- bacterial polymer particles in accordance with the present invention are obtained.

[0035]

As an anti- bacterial metal component and hydrophilic polymer particles

are chemically bound in the anti- bacterial polymer particles in accordance with the present invention, a high degree of anti- bacterial activity can be displayed for a long period of time. Especially since they are constituted with a hydrophilic polymer, they absorb water, and the particles are swollen under a high humidity environment in which recent (sic: note by translator: a mistake of bacteria) and microorganisms tend to grow and proliferate, the anti- bacterial metal component in particles tends to be more readily released, and thus they offer an environmental response property. Especially, with micro particles (for example, particles of a nano size), the distance for an anti- bacterial metal component inside particles to reach the particle surface is short, and thus it is possible to improve the contact efficiency between an anti- bacterial metal component and bacteria and microorganisms by increasing the surface area of particles. Furthermore, just by immersing hydrophilic polymer particles whose anti- bacterial activity has been reduced, in a solution (aqueous solution) containing an anti- bacterial metal component , it is possible to regenerate them. Furthermore, an anti- bacterial metal

component can be stably carried, and even if irradiated with an ultraviolet ray, no discoloring takes place. Furthermore, since the carrier is an organic polymer, it is possible to form a highly anti- bacterial coating with high affinity to both hydrophobic and hydrophilic organic polymers and high dispersability of the polymer particles. Therefore, the anti-bacterial polymer in accordance with the present invention is useful in making an anti- bacterial resin composition by combining with a resin (for example, a resin used in an ultraviolet ray setting coating or a resin used in a water solution coating).

[0036]

[Anti- bacterial resin composition] For an anti- bacterial resin composition, a resin can be selected from a broad range of resins depending on use. As a resin, mention may be made of a thermoplastic resin [an olefin series resin (poly ethylene, poly propylene, poly ethylene modified with a carboxylic group, an acid anhydride group, and an epoxy group, etc., and modified poly propylene, etc.), an acryl series resin (poly methacrylic acid methyl, an acryl resin containing a carboxylic group, an

acryl resin containing a hydroxyl group, an acryl resin containing an epoxy group, etc.), a styrene series resin (poly styrene, AS resin, ABS resin, a copolymer of styrene and a (metha) acryl series monomer, etc.), a vinyl acetate series resin (poly vinyl acetate, an ethylene – vinyl acetate copolymer, a vinyl acetate – vinyl chloride copolymer, etc.), a vinyl alcohol series polymer (poly vinyl alcohol, an ethylene – vinyl alcohol copolymer, etc.), a vinyl chloride series resin (poly vinyl chloride, etc.), a polyester resin (poly alkylene terephthalate, poly alkylene naphthalate, a copolymerized poly ester resin, a modified poly ester resin, etc.), a poly urethane resin, a poly amide resin, rubber, etc.], a thermo-setting resin [an epoxy resin, a phenol resin, an urethane resin, an unsaturated polyester resin, a vinyl ester resin, a diallyl phthalate resin, a silicone resin, an amino resin (an urea resin, a melamine resin, etc.), etc.], a light setting resin [a light setting oligomer such as epoxy (metha) acrylate, urethane (metha) acrylate, and poly ester (metha) acrylate, a multi-functional (metha) acrylate, a light setting monomer such as a nitrogen-containing monomer], etc. These resins can be used alone or in a

combination of 2 or more kinds. Such resins can be a water- soluble resin, a water- soluble resin or an organic solvent – soluble resin. Furthermore, such resins can be used as a water dispersion resin (emulsion, latex, etc.), a non water dispersion resin (organo sol).

[0037]

The resin compositions in accordance with the present invention can be an anti- bacterial resin composition for molding containing a resin for molding which can be used for extrusion molding, injection molding, etc., or a resin composition containing a resin for adhesion, however, are preferably a resin composition for coating containing a resin for coating (binder resin) such as a paint. When a coating (coating film) containing anti- bacterial polymer particles is formed, a high degree of anti- bacterial activity can be retained effectively on the surface of a product for a long period of time. The forms of resin composition for coating can be any of the following : a powder coating agent constituted with granules, an aqueous coating agent in which the solvent is an aqueous solvent, a solvent type coating agent in which the solvent is an organic solvent, and

a non- solvent type coating such as an ultraviolet setting type paint. The amount of use of the anti- bacterial polymer particles can be selected from a wide range: for example, in terms of a solid conversion, about 0.01 to 200 parts by weight with respect to 100 parts by weight of a resin, preferably about 0.1 to 100 parts by weight, and more preferably about 0.5 to 50 parts by weight. The thickness of the coated film (anti- bacterial layer) can be selected from a broad range, for example, about 1 to 500 μm, more preferably about 5 to 300 μm.

[0038]

The anti- bacterial composition in accordance with the present invention may contain various types of additives such as a stabilizer (such as an oxidation preventing agent, an ultraviolet ray absorbing agent, and a thermal stabilizer), a plasticizer, an electric charge preventing agent, a flame retardant, a dispersion agent, a surface active agent, a filler, a coloring agent, a viscosity adjusting agent, an anti- corrosive agent, an anti- fungus agent, and a leveling agent.

[0039]

The anti- bacterial resin composition (or a resin composition for coating) can be prepared by mixing the above - mentioned anti- bacterial polymer particles, a resin or a binder resin, and if necessary a solvent or an additive, etc. For the preparation of a resin composition, depending on a form of a resin composition, use may be made of conventional equipment such as a kneading machine, a dispersion machine and a mixer.

[0040]

A coated film may be formed by coating a base material with a resin composition for coating by a conventional coating process, followed by drying (if necessary, thermal setting) or light irradiation (ultraviolet ray irradiation). As a base material, use may be made of paper, timber, plastic, ceramics containing glass, a metal, etc.

[0041]

When the anti- bacterial polymer particles (anti- bacterial agent) in accordance with the present invention are used for a coating agent, it is possible to uniformly and easily disperse the anti- bacterial agent, the dispersion stability becomes high and it is possible to prevent

precipitation and separation from taking place. Therefore, it is possible to effectively display the activity of an anti- bacterial agent even if use is made of a small quantity of an anti- bacterial agent. Furthermore, since the affinity and adhesion to an organic binder are high, it becomes possible to form a highly transparent coating film having uniformity and high mechanical strength.

[0042]

[Effects of the Invention]

With the present invention, as an anti- bacterial metal component of an anti- bacterial agent is chemically bound to hydrophilic polymer particles having a cross linking structure, in spite of the fact that use is made of an inorganic anti- bacterial metal component, a high degree of anti- bacterial activity can be displayed for a long period of time, and thus the durability is high. In addition, since the polymer particles are hydrophilic, the anti-bacterial activity can be effectively displayed as the humidity or a water content increases, and thus it has an environmental response property. Furthermore, when used as a resin composition such as a coating agent,

such an anti- bacterial agent is excellent in dispersion property, affinity to an organic polymer, and coating property.

[0043]

[Examples Embodying the Invention]

In the following, we shall explain the present invention in more detail by referring to some examples embodying the invention, however, it should be understood that the present invention is not limited to these examples embodying the invention.

Example 1

[Preparation of fine cross linking hydrophilic polymer particles]

A mixture solution of 4 g (0.056 mol, 72.2 mol %) of acryl amide, 2.4 g (0.0156 mol, 20.1 mol %) of methylene bis- acryl amide and 1.6 g (0.006 mol, 7.7 mol %) of 4 – (N, N- diethyl dithio carbamate) styrene was added to a mixture solvent of 86 ml of ethanol and 6 ml of water, and by using 0.05 g of azo bis iso- butyronitrile, a precipitation polymerization was allowed to take place at a temperature of 60 °C in an argon atmosphere for 17 hrs. In this reaction, after heating to 60 °C, the

polymerization system became turbid in about 2.5 hrs, and polymer particles are produced.

[0044]

[Hydrolysis]

A mixture solution of 100 ml of ethanol, 50 ml of water and 2 g of sodium hydroxide was added to the reaction mixture solution, and after hydrolysis by stirring it at a temperature of 70 °C for 5 hrs in an argon atmosphere, it was subjected to centrifugal separation and the precipitated particles were washed twice with a mixture solvent of 100 ml of ethanol and 100 ml of water. In order to produce a mercapto group, water was added to the precipitated particles, 1 – N hydrochloric acid was then added thereto, adjusting the pH value to about 5, and hydrolysis was allowed to take place by stirring for 24 hrs. Following this, the mixture solution was subjected to centrifugal separation, the precipitated particles were washed three time with a mixture solvent of 100 ml of ethanol and 100 ml of water, followed by washing twice with 150 ml of water.

[0045]

[Preparation of silver complex -carrying polymer particles]

A mixture solution of 1.05 g of silver nitrate (0.006 mol) and 150 ml of water was added to the washed particles precipitated, and it was stirred at room temperature for 2 hrs. Then the particles changed the color to light orange. The mixture solution was subjected to centrifugal separation, the particles precipitated were washed once with 150 ml of water, and twice with 150 ml of methanol, and dried under a reduced pressure. Thus, silver complex -carrying polymer particles were prepared (average particle diameters from about 60 to 90 nm). (yield 7.8 g (when converted into dry solids), water content 14.9 % by weight, silver content 22.8 % by weight, yield 89.9 %).

[0046]

Example 2

[Preparation of cross linking hydrophilic polymer particles]

A mixture solution of 4 g (0.056 mol) of acryl amide, 2.4 g (0.0156 mol) of methylene bis- acryl amide and 1.6 g (0.0152 mol) of 4 – vinyl

pyridine was added to a mixture solvent of 86 ml of ethanol and 6 ml of water, and by using 0.05 g of azo bis iso- butyronitrile, a precipitation polymerization was allowed to take place at a temperature of 60 °C in an argon atmosphere for 17 hrs. In this reaction, after heating to 60 °C, the polymerization system became turbid in about 2.5 hrs, and polymer particles are produced. The reaction mixture solution was subjected to centrifugal separation and the particles thus precipitated were washed twice with 150 ml of water.

[0047]

[Preparation of silver complex -carrying polymer particles]

A mixture solution of 2.58 g of silver nitrate (0.0152 mol) and 150 ml of water was added to the washed particles precipitated, and it was stirred at room temperature for 2 hrs. The mixture solution was subjected to centrifugal separation, the particles precipitated was washed twice with 150 ml of methanol, and dried under a reduced pressure. Thus, silver complex -carrying polymer particles were prepared (average particle diameters from about 90 to 120 nm). (yield 8.6 g (when converted into

dry solids), water content 13.3 % by weight, silver content 35.2 % by weight).

[0048]

Example 3

[Preparation of cross linking hydrophilic polymer particles]

A mixture solution of 4.5 g (0.063 mol) of acryl amide, 2.4 g (0.0156 mol) of methylene bis- acryl amide and 1.1 g (0.0152 mol) of acrylic acid was added to a mixture solvent of 86 ml of ethanol and 6 ml of water, and by using 0.05 g of azo bis iso- butyronitrile, a precipitation polymerization was allowed to take place at a temperature of 60 °C in an argon atmosphere for 17 hrs. In this reaction, after heating to 60 °C, the polymerization system became turbid in about 0.5 hrs, and polymer particles are produced. The reaction mixture solution was subjected to centrifugal separation and the particles thus precipitated were washed twice with 150 ml of water.

[0049]

[Preparation of silver complex -carrying polymer particles]

A mixture solution of 2.58 g (0.0152 mol) of silver nitrate and 150 ml of water was added to the washed particles precipitated, and it was stirred at room temperature for 2 hrs. The mixture solution was subjected to centrifugal separation, the particles precipitated was washed twice with 150 ml of methanol, and dried under a reduced pressure. Thus, silver complex -carrying polymer particles were prepared (average particle diameters from about 90 to 120 nm). (yield 11.5 g (when converted into dry solids), water content 13.9 % by weight, silver content 25.7 % by weight).

[0050]

[Evaluation of anti- bacterial activity]

The anti- bacterial activity was evaluated as follows by the minimum growth inhibition concentration (MIC, ppm) according to the standard method of the Japanese Society of Chemotharapy.

(1) Specimen

The silver complex – carrying polymer particles obtained in Example 1 through Example 3

Example for Comparison 1 : commercially available silver silica gel anti-bacterial agent (silver ion quantity, about 3 % by weight)

Example for Comparison 2 : commercially available silver zeolite series anti- bacterial agent (silver ion quantity, about 3 % by weight)

(2) Bacterial stocks used

Staphylococcus aureus : staphylococcus aureus 209P JC -1

Escherichia coli : Escherichia coli NIHJ JC -2

(3) Culture medium

A bouillon culture medium for sensitivity measurement and an agar- agar culture medium for sensitivity disk were used.

(4) Test method

As the specimens were insoluble, they were each suspended, and suspensions of a concentration 10 times the test concentration were prepared. Here in testing, a culture medium and a specimen suspension were mixed for use at a ratio of 9 parts by volume of a culture medium per one part by volume of a specimen suspension. On the other hand, the test bacteria were cultivated over night at 37 ° C by use of the sensitivity

bouillon culture medium and then it was diluted appropriately with the same culture medium, thereby preparing 10^6 cfu / ml test bacteria solution. The results are shown in Table 1.

[0051]

[Table 1]

Table 1

Bacterial Stock	Min. Growth Inhibition Concentration (MIC, ppm)				
	Ex. 1	Ex. 2	Ex. 3	Ex. for Comp. 1	Ex. for Comp. 2
S. aureus	1000	250	2000	>8000	4000
E. coli	500	250	2000	>8000	4000

As can be clearly seen from Table 1, the anti- bacterial polymer particles of Example 1 through Example 3 show high anti- bacterial activities in comparison with the commercially available products.

[0052]

Example 4

One part by weight of the silver complex- carrying polymer particles obtained in Example 2 and 99 parts by weight of an ultraviolet setting type paint (made by Toa Gosei K., K., Co., Ltd., Acronix UV – 3701) were mixed, polyethylene terephthalate film was coated with the dispersion mixture solution thus obtained by use of a bar coater, and a hardened film was obtained by irradiating it with an ultraviolet ray for 10 min by use of a high pressure mercury lamp.

Example for Comparison 3

In place of the silver complex- carrying polymer particles of Example 2, use was made of the anti- bacterial agent of Example for Comparison 2, but otherwise, a hardened film was formed in a manner similar to the above.

[0053]

Example 5

One part by weight of the silver complex- carrying polymer particles obtained in Example 2 and 99 parts by weight (when converted into solids) of an aqueous emulsion paint (made by Toa Gosei K., K., Co.,

Ltd., Aron NS – 1200) were mixed, polyethylene terephthalate film was coated with the dispersion mixture solution thus obtained by use of a bar coater, and a coated film was obtained by drying it at room temperature.

Example for Comparison 4

In place of the silver complex- carrying polymer particles of Example 2, use was made of the anti- bacterial agent of Example for Comparison 2, but otherwise, a coated film was formed in a manner similar to the above.

[0054]

And the anti- bacterial activity of the coated films against the above - mentioned bacteria was studied in the following manner. After cultivating staphylococcus aureus 209P JC 1 and Escherichia coli NIHJ JC -2 in normal bouillon culture media (NB, Eiken) at 37 ° C for 18 to 20 hrs, appropriate dilution was further made with a normal bouillon culture medium (NB, Eiken) diluted to 1/ 500 in concentration, and thus a test bacteria solution of 10^5 cfu /ml was prepared. One ml of the test bacteria solution was put in a plastic dish of 35 mm in diameter with graduation (Sumilon), the above - mentioned specimen coated film was allowed to

be in contact with the test bacterial solution with the film surface underside, the dish was covered with a lid, sealed and left undisturbed at room temperature (25 ° C) for 24 hrs. In addition, as a control, by using the bacterial solution (untreated) only, an operation similar to the above was repeated. The bactericidal action was measured by the mixture dilution method by use of a normal agar- agar culture medium (NA, Eiken) basedon the counts of the number of bacteria at the time of starting and that 24 hrs thereafter, and thus it was evaluated from the changes in number of bacteria. Table 2 gives the anti- bacterial activity of the coated films.

[0055]

[Table 2]

Table 2

	Types of bacterial stocks	Contact time	
		0 h	24 h
Ex. 4	S. aureus	4.3×10^5	< 10

Ex. for Comp. 3		4.3×10^5	1.5×10^5
Ex. 5		4.3×10^5	< 10
Ex. for comp. 4		4.3×10^5	3.8×10^5
Control (untreated)		4.3×10^5	7.7×10^5
Ex. 4	E. coli	1.7×10^5	< 10
Ex. for Comp. 3		1.7×10^5	1.1×10^5
Ex. 5		1.7×10^5	< 10
Ex. for Comp. 4		1.7×10^5	3.5×10^5
Control (untreated)		1.7×10^5	1.5×10^5

As can be clearly seen from Table 2, the anti- bacterial polymer particles

of the examples embodying the invention show high anti- bacterial activities in comparison with the commercially available products. Here, the hardened film formed in Example 4 was a hardened film with high transparency though slightly colored in yellow. On the other hand, the hardened film formed in example for Comparison 3 was colored in red brown, and the transparency was reduced. In this manner, the anti-bacterial polymer particles of Example 2 were stable with respect to an ultraviolet ray probably due to the presence of the silver ion as a complex. In addition, as the anti- bacterial polymer particles of Example 2 were very small in particle diameters, and as the particles are formed with an organic polymer, there is no difference in index of refraction between them and a base resin (ultraviolet setting type resin), and the degree of transparency is high. On the other hand, the anti- bacterial agent of Example for Comparison 2 is colored due to low stability of a silver ion, and the particle diameters are as large as 1 to 3 μm. Furthermore, as the difference in index of refraction from the base resin is large, the degree of transparency is reduced.

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